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Analysis of sub-3 nm particle growth in connection with sulfuric acid in a boreal forest

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We analyzed nanoparticle growth during new-particle-formation events based on ten years of measurements carried out at a boreal forest site in Hyytiälä, Finland, concentrating on the sub-3 nm particles and the role of sulfuric acid in their growth. Growth rates of 1.5–3 nm diameter particles were determined from ion spectrometer measurements and compared with parameterized sulfuric acid concentration and other atmospheric parameters. The calculated growth rates from sulfuric acid condensation were on average 7.4% of the observed growth rates and the two did not correlate. These suggest that neither sulfuric acid monomer condensation nor coagulation of small sulfuric acid clusters was the primary growth mechanism in these atmospheric conditions. Also no clear sign of organic condensation being the single main growth mechanism was seen. These observations are consistent with the hypothesis that several factors have comparative roles in the sub-3 nm growth.

Introduction

Atmospheric aerosol particles affect climate directly by scattering and absorbing radiation (Lesins *et al*. 2002), and indirectly by acting as cloud condensation nuclei (CCN) and affecting properties and lifetimes of clouds (Lohmann and Feichter 2005). Regional new-particle-formation (NPF) events, i.e. formation of nanometer sized particles by gas-to-particle conversion from atmospheric trace gases followed by particle growth, are frequently observed in the atmosphere in a wide range of environments (Kulmala *et al*. 2004). Regional NPF events produce typically high number of small nucleation mode particles and, thus, increase significantly the total number concentration of aerosol particles (Merikanto *et al*. 2009). However, these particles can have an effect on the CCN number concentration only if they grow tens of nanometers in diameter (Dusek *et al*. 2006). While the particles are growing, the number concentration of nucleation mode particles is decreasing due to coagulation scavenging. Therefore, the longer the growth to the CCN sizes takes the larger is the fraction of the nucleation mode particles that is lost by the coagulation (Kerminen and Kulmala 2002, Kuang *et al*. 2009). Especially the growth rate in the smallest particle sizes has a great effect on the survival of the newly-formed

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particles to the CCN sizes due to the strong size dependence of the coagulation loss rate.

Several studies have found strong connection between atmospheric NPF and gas-phase sulfuric acid, and the first step of NPF is widely considered to be nucleation starting with clustering of sulfuric acid molecules and bases, ammonia or amines, as neutralizing compounds (Weber *et al*. 1995, Kuang *et al*. 2008, Kurtén *et al*. 2008, Ortega *et al*. 2008, Sipilä *et al*. 2010, Almeida *et al*. 2013, Kulmala *et al*. 2006, 2013). The growth of the particles, on the other hand, can be explained in most environments only partly by the condensation of sulfuric acid (Weber *et al*. 1997, Birmili *et al*. 2003, Kulmala *et al*. 2004, Boy *et al*. 2005, Fieldler *et al*. 2005, Stolzenburg *et al*. 2005, Riipinen *et al*. 2011, Kuang *et al*. 2010, 2012), exception being environments with elevated sulfuric acid concentrations such as polluted urban environments (Birmili *et al*. 2003, Stolzenburg *et al*. 2005, Yue *et al*. 2010). There is strong evidence that in many cases organics make a major contribution to the nanoparticle growth at least after the first few nanometers of diameter growth (Kulmala *et al*. 1998, O'Dowd *et al*. 2002, Smith *et al*. 2008, 2010, Riipinen *et al*. 2009, Laitinen *et al*. 2011, Riipinen *et al*. 2012, Bzdek *et al*. 2013, Pennington *et al*. 2013). Already in 1998 Kulmala *et al*. (1998) predicted that low volatile organics are responsible for the condensational growth of the atmospheric newly born aerosol particles. Recent studies have shown that organic compounds may be involved already in the first steps of new-particle formation, even at atmospheric concentrations (Metzger *et al*. 2010, Riccobono *et al*. 2014). Furthermore, extremely low volatile organic compounds (ELVOC) were recently detected in the atmosphere (Ehn *et al*. 2014). In the light of these new results, it is reasonable to expect that organic compounds could contribute significantly also to the growth of sub-3 nm particles, even though previous studies had not found clear evidence of this (Hirsikko *et al*. 2005, Yli-Juuti *et al*. 2011). On the other hand, studies analyzing contribution of sulfuric acid to the nanoparticle growth typically consider sulfuric acid monomer condensation neglecting the effect of sulfuric acid containing clusters. It has been hypothesized that the coagulation of sulfuric acid containing clusters with the growing nanoparticles could affect the nanoparticle growth (Weber *et al*. 1997). In fact, recent results from the experiments in the CLOUD chamber suggest that the contribution of sulfuric acid on the growth might be underestimated when only condensation of sulfuric acid monomers is taken into account without considering the sulfuric acid clusters, and such hidden sulfuric acid may increase the nanoparticle growth rate drastically (Lehtipalo *et al*. 2016). Also field observations at a South African site suggest that sulfuric acid may account for a larger fraction of the nanoparticle growth than expected based on gas phase sulfuric acid monomer concentration (Vakkari *et al*. 2015).

In this paper, we analyze atmospheric nanoparticle growth at the SMEAR II measurement station in Hyytiälä with the focus on the first steps of the growth, the sub-3 nm size range, and the connection to sulfuric acid. Previous studies comparing sulfuric acid gas phase concentration and nanoparticle growth rates at Hyytiälä have reported that, based on its gas phase concentrations, sulfuric acid condensation can explain typically from few percents to few tens of percents of the observed growth rate (Boy *et al*. 2005, Riipinen *et al*. 2011, Nieminen *et al*. 2014). Previous studies have concentrated on the growth of particles larger than 3 nm. While it is concluded that organic trace gases play a major role in the growth of the larger nucleation mode particles at Hyytiälä, the observations for sub-3 nm growth have been inconclusive (Yli-Juuti *et al*. 2011). Due to the recent observation of the role of sulfuric acid in sub-3 nm growth in the laboratory environment and the role of organics in nucleation, re-examination of atmospheric observations with extended data set is justified. The aim of this study was to investigate using an extended atmospheric data set whether sulfuric acid can explain a major fraction of the sub-3 nm particle growth in a boreal forest environment.

Methods

Measurements were carried out at the SMEAR II site in Hyytiälä, southern Finland (Hari and Kulmala 2005). Hyytiälä is a rural measurement site at the boreal forest region. In this study, we use atmospheric data collected between April 2003 and June 2013.

Calculation of growth rate from measurements

Particle size distributions down to 0.8 nm were measured using an Air Ion Spectrometer (AIS; manufactured by Airel Ltd., Estonia; detailed description in Mirme *et al*. 2007) and Balanced Scanning Mobility Analyzer (BSMA; manufactured by Airel Ltd., Estonia; detailed description in Tammet 2006). Measurements with BSMA were carried out throughout the study years whereas there was a long measurement break with AIS between July 2007 and January 2010. The detection ranges of these ion spectrometers (0.8–40 nm for AIS and 0.8–7 nm for BSMA) enable the study of sub-3 nm particle growth. However, both instruments detect only naturally-charged particles. All diameters are reported as mobility-equivalent Millikan-Fuchs diameter (Mäkelä *et al*. 1996).

The diameter growth rate (GR) of particles was calculated using the maximum concentration method (Lehtinen *et al*. 2003, Hirsikko *et al*. 2005, Yli-Juuti *et al*. 2011), in which first the moment of maximum concentration during the NPF event is determined for each size bin within the size range of interest, and then a straight line is fitted to these time and diameter data pairs giving the GR as the slope of the line. The sub-3 nm particle GR ($GR_{1.5–3}$) was obtained by fitting to the size range from 1.5 nm to 3 nm. The GR values from the two instruments based on negatively and positively charged particles were averaged for each NPF event in order to have one representative value for $GR_{1.5–3}$. Therefore, the value of $GR_{1.5–3}$ for each NPF event is based on one to four growth rate values depending on from which instrument and polarity it was possible to determine GR. The uncertainty in the $GR_{1.5–3}$ values calculated with this method is estimated to be on average 25%, and the negatively-charged particle distribution gives lower values than the positively-charged particle distribution (Yli-Juuti *et al*. 2011). The GR was calculated based on size distributions of charged particles and, therefore, the calculated values of GR may differ from the GR of neutral particles. However, Kulmala *et al*. (2013) indicated that GR is similar for neutral and charged particles in Hyytiälä, since there neutral particles and clusters dominate the total particle number concentration.

In the studied period, there were 281 new-particle-formation events for which the calculation of $GR_{1.5–3}$ was successful, and during 259 of these cases also the other data used in this study were available.

Sulfuric acid concentration

The sulfuric acid concentration ($[H_2SO_4]$) was calculated using the parameterization presented by Petäjä *et al*. (2009), which is based on the gas phase concentration of sulfur dioxide ($[SO_2]$), UVB radiation intensity (UVB) and condensation sink of sulfuric acid on aerosol particles (CS):

$$[\mathrm{H_2SO_4}] = k\frac{[\mathrm{SO_2}]\times \mathrm{UVB}}{\mathrm{CS}}, \quad (1)$$

where $k = 8.4 \times 10^{-7} \times \mathrm{UVB}^{-0.68}$ m^2 W^{-1} s^{-1} is an empirically-derived scaling factor.

The above parameterization of the sulfuric acid concentration has been obtained by fitting to measured concentration data by Chemical Ionization Mass Spectrometer (CIMS) from the spring measurement campaign in March–June 2007. The calculated sulfuric acid concentration might, therefore, have a greater uncertainty under atmospheric conditions other than those during that spring campaign (Mikkonen *et al*. 2011).

Organic concentration

The monoterpene concentration ($[\mathrm{MT}]_{\mathrm{model}}$) was calculated according to a parameterization based on the daily-average temperature (Lappalainen *et al*. 2009):

$$[\mathrm{MT}]_{\mathrm{model}} = a\exp(bT), \quad (2)$$

where T is the ambient temperature and the fitted parameters have the values of $a = 0.062$ ppb$_v$ and $b = 0.078$ °C^{-1}.

The concentration of oxidized organic gas phase compounds ([OxMT]) was calculated as the sum of the concentrations of first-order OH^- and O_3-oxidation products of monoterpenes according to

$$[\mathrm{OxMT}] = \frac{k_{\mathrm{OH}}[\mathrm{OH}]_{\mathrm{model}}[\mathrm{MT}]_{\mathrm{model}} + k_{\mathrm{O_3}}[\mathrm{O_3}][\mathrm{MT}]_{\mathrm{model}}}{\mathrm{CS}}, \quad (3)$$

where k_{OH} and k_{O3} are the reaction rate coefficients between monoterpenes and OH and O_3, respectively, $[\mathrm{OH}]_{\mathrm{model}}$ is the OH concentration calculated based on Petäjä *et al*. (2009) and $[O_3]$ is the measured O_3 concentration. The condensation sink of the organics was approximated with that of sulfuric acid. The average monoterpene composition at Hyytiälä was used for estimating the reaction rate coefficients: $k_{\mathrm{OH}} = 7.5 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1} and $k_{\mathrm{O3}} = 1.4 \times 10^{-17}$ cm^3 molecules^{-1} s^{-1} (Hakola *et al*. 2003, Yli-Juuti *et al*. 2011).

Growth rate from sulfuric acid condensation

The theoretical growth rate from sulfuric acid condensation, $GR_{H_2SO_4}$, was calculated based on the mass flux equations presented by Lehtinen and Kulmala (2003) (*see* also Nieminen *et al*. 2010) by assuming the equilibrium vapor pressure of sulfuric acid to be negligible, providing the kinetic limit of sulfuric acid condensation. A particle diameter of 2 nm was used for the calculation of $GR_{H_2SO_4}$. $GR_{H_2SO_4}$ was calculated for each NPF event based on the data measured during the time of the particle growth from 1.5 to 3 nm. This period was defined to start one hour before and end one hour after the time during which the $GR_{1.5–3}$ was determined from the size distribution measurements.

The theoretical growth rate was also calculated by assuming sulfuric acid to be neutralized in the particle phase by ammonia or dimethylamine (DMA) with base:acid molar ratio of 2:1. In these cases, two DMA or ammonia molecules were assumed to condense onto the particles for each condensing sulfuric acid molecule. This approximation was used to obtain the upper limit of the growth rate explained by the combined condensation of sulfuric acid and basic compounds. However, theoretically the contribution of bases on the growth is expected to depend on the gas phase concentrations of the bases (Yli-Juuti *et al*. 2013).

The effect of particle-phase water on the growth rate was tested by calculating the equilibrium water content of sulfuric acid aqueous solution particles using the Extended Aerosol Inorganics Model (E-AIM; Clegg *et al*. 1992, 1998, Wexler and Clegg 2002; available at http://www.aim.env.uea.ac.uk/aim/aim.php). The gas-liquid equilibrium calculations were corrected for the surface curvature effect using the surface tension of the solution from E-AIM and pure liquid water density of 1000 kg m^{-3}. The water content was calculated for each NPF event based on the measured relative humidity and assuming a temperature of 283.15 K. These calculations are approximative because the bulk thermodynamics-based E-AIM may not fully capture the hydration effect of the smallest particles (Henschel *et al*. 2014). The calculated water to sulfuric acid molar ratio was used as an estimate of how many water molecules are condensing per each sulfuric acid molecule. The resulting water to sulfuric acid ratio varied from 2.8 to 5.1 with a median of 3.8. Therefore, the theoretically-calculated GR from sulfuric acid and water condensation (at maximum about 5 water molecules per each sulfuric acid molecule) were lower or similar to the growth rates from condensation of sulfuric acid and DMA (2 DMA molecules per each sulfuric acid molecule) and thus the growth rate calculated with DMA is presented in the figures as the upper limit of the sulfuric acid condensation-driven GR.

The fraction of GR explained by sulfuric acid condensation was calculated by dividing the theoretical value of $GR_{H_2SO_4}$ by the observed value of $GR_{1.5–3}$. This ratio is similar to the inverse of the growth enhancement factor used in some other studies (e.g. Kuang *et al*. 2010). However, the assumptions made in calculating $GR_{H_2SO_4}$ cause some variability to its value depending on whether the diffusivity of the particle and the dimensions of the vapor molecule are taken into account and how the sulfuric acid diffusivity is calculated.

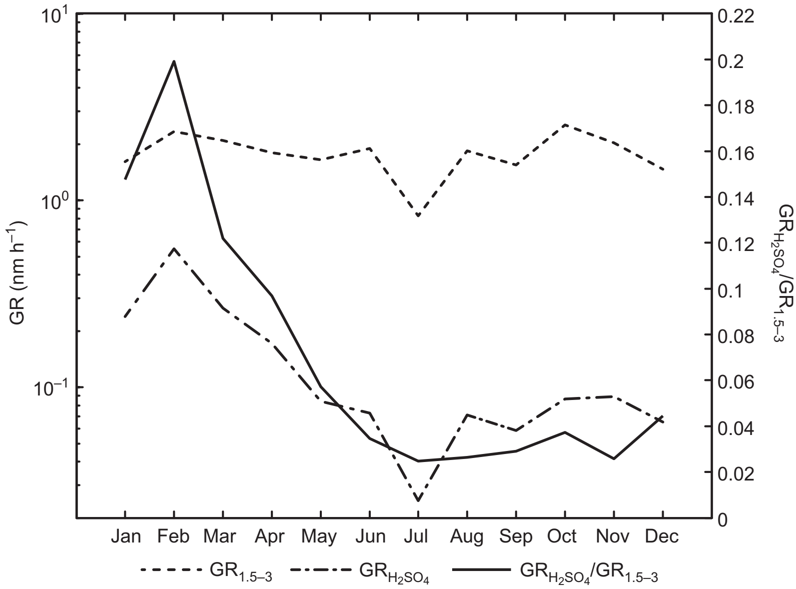

Fig. 1. Monthly median values of the measured GR of 1.5–3 nm particles ($GR_{1.5-3}$), calculated growth rate based on pure sulfuric acid condensation ($GR_{H_2SO_4}$) and fraction of $GR_{1.5-3}$ that can be explained by sulfuric acid condensation ($GR_{H_2SO_4}/GR_{1.5-3}$). Data are averaged over years 2003–2013.

Results and discussion

Seasonal variation of $GR_{1.5-3}$, $GR_{H_2SO_4}$ and fraction of the growth explained by sulfuric acid

The monthly-median values of the measured growth rates of 1.5–3 nm particles ($GR_{1.5-3}$) averaged over the 10 years of data were rather similar between different months (Fig. 1). The only month deviating from the overall pattern was July when the monthly-median value of $GR_{1.5-3}$ was smaller (0.8 nm h^{-1}) as compared with the values for the other months (1.5–2.5 nm h^{-1}).

The calculated growth rate due to sulfuric acid condensation ($GR_{H_2SO_4}$) depended mainly on the gas phase concentration of sulfuric acid and followed its seasonal pattern, with the highest values observed in winter and lowest values in summer (Fig. 1). Interestingly, also the $GR_{H_2SO_4}$ had its lowest monthly-median value in July.

The seasonal variation of the fraction of growth rate explained by sulfuric acid condensation ($GR_{H_2SO_4}/GR_{1.5-3}$) followed to a large extent the variation of sulfuric acid concentration, since there was no clear seasonal variation in $GR_{1.5-3}$ (Fig. 1). On the monthly-average basis, sulfuric acid condensation could explain 2%–20% of the observed nanoparticle growth rate.

$GR_{1.5-3}$ and sulfuric acid concentration

The measured values of $GR_{1.5-3}$ were in most cases higher than what can be explained by condensation of sulfuric acid, or by sulfuric acid together with neutralizing amine or ammonia (Fig. 2). The few exceptions when the theoretical growth rate reached or exceeded the measured value were mostly on cold days when the sulfuric acid concentration was elevated. The values of $GR_{1.5-3}$ showed no clear increase with an increasing sulfuric acid concentration (Fig. 2), so it is highly unlikely that sulfuric acid would be the only key compound in the sub-3 nm particle growth even if the absolute values of sulfuric acid were higher than estimated as a result of the hidden sulfuric acid in the molecular clusters (Lehtipalo *et al*. 2016). The correlation coefficient between $GR_{1.5-3}$ and sulfuric acid concentration was $r = 0.14$ ($p = 0.02$). Pearson's linear correlation coefficients were calculated based on the logarithms of the variables (concentrations and growth rate related parameters), and all of these variables were approximately log-normally distributed.

There was some increase in the values of $GR_{1.5-3}$ with an increasing sulfuric acid concentration when the measurement points were binned according to sulfuric acid concentration

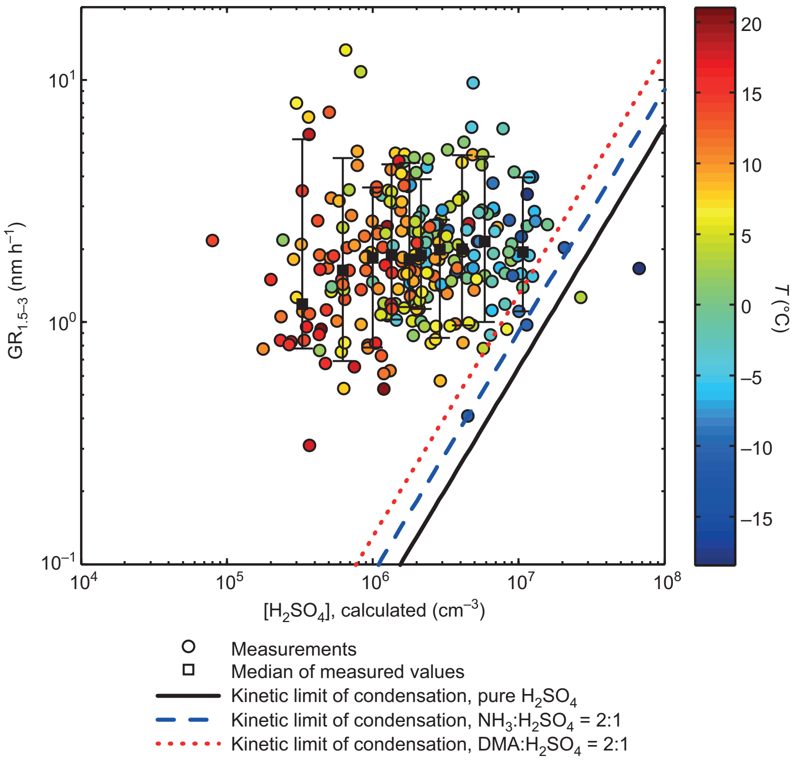

Fig. 2. Observed growth rate of 1.5–3 nm particles *versus* the modeled sulfuric acid concentration and ambient temperature during the period for which the $GR_{1.5-3}$ was determined. Lines represent the kinetic limits (= no evaporation) of growth rate of 2 nm particle calculated based on pure sulfuric acid condensation (black line) and condensation of sulfuric acid and subsequent neutralization by ammonia (blue dashed line) or DMA (red dotted line). The measured data points were divided based on sulfuric acid concentration into ten bins with an equal number of data points. The medians (squares) and the 10th/90th percentiles (error bars) of GR in each bin are also presented.

(squares in Fig. 2). This is reasonable because some of the growth is expected to be due to sulfuric acid condensation albeit other factors are also affecting the growth.

Fraction of $GR_{1.5-3}$ explained by sulfuric acid

The fraction of sub-3 nm growth that can be explained by sulfuric acid condensation increased with increasing sulfuric acid concentration (Fig. 3). When sulfuric acid concentration was lower than 10^6 cm^{-3}, condensation of sulfuric acid could explain at the most 8.0% of the growth (median for the 67 cases was 2.3%). When sulfuric acid concentration was higher than 10^7 cm^{-3}, condensation of sulfuric acid could explain at least 19.3% of the growth (median for the 17 cases was 40.9%). As noted earlier, the variation in the fraction of $GR_{1.5-3}$ that can be explained by sulfuric acid is to a large extent controlled by the variation in the sulfuric acid concentration because the measured values of $GR_{1.5-3}$ values did not vary greatly. The clear increase in the fraction of growth that can be explained by sulfuric acid condensation with an increasing sulfuric acid concentration indicates that the variability in $GR_{1.5-3}$ between different days was controlled by factors other than the sulfuric acid condensation. On average, pure sulfuric acid condensation could explain 7.4% (median) of the observed growth.

The fraction of growth that can be explained by sulfuric acid did not show a clear connection with the parameter describing the oxidized organic concentration (Fig. 3). The ratio $GR_{H_2SO_4}$/$GR_{1.5-3}$ increased with an increasing sulfuric acid concentration for a fixed oxidized organic concentration but did not vary systematically with the oxidized organic concentration for a fixed sulfuric acid concentration. The correlation coefficient between the oxidized organic concentration and fraction of growth that can be explained by sulfuric acid was r = –0.46 (p << 0.001). This negative correlation results likely from the positive correlation between the sulfuric acid concentration and fraction of growth that can be explained by sulfuric acid condensation (r = 0.85, p << 0.001), combined with the negative

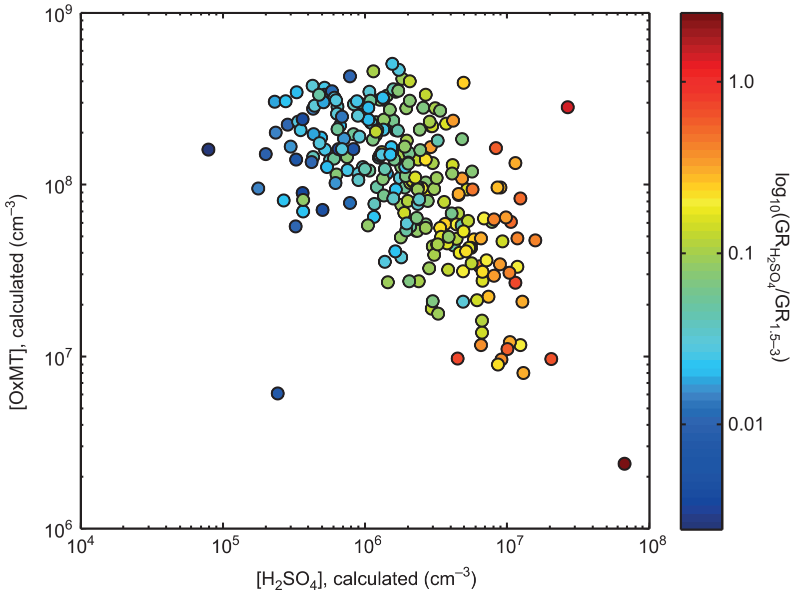

Fig. 3. Fraction of sub-3 nm growth rate that can be explained by sulfuric acid condensation (color of data points) as a function of calculated concentration of monoterpene oxidation products and sulfuric acid during the growth time.

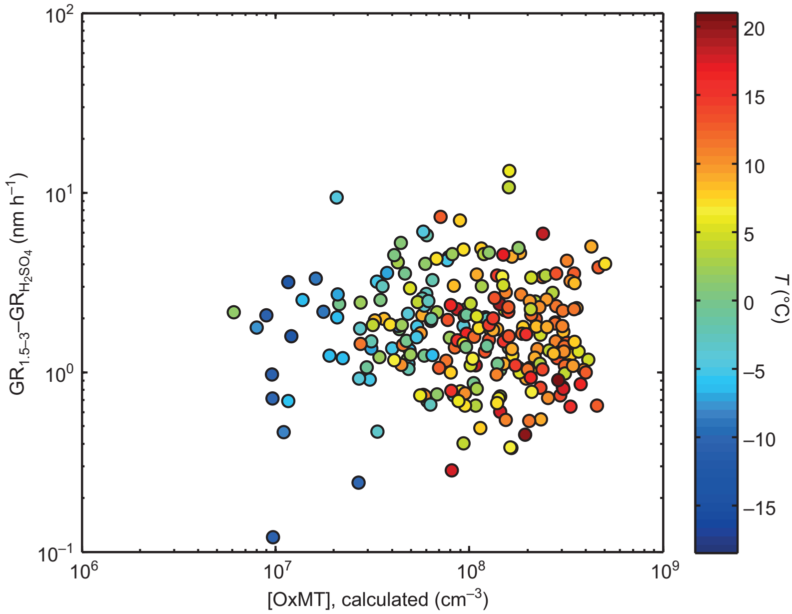

Fig. 4. Difference between the observed growth rate of 1.5–3 nm particles ($GR_{1.5-3}$) and growth rate that can be explained by sulfuric acid condensation ($GR_{H_2SO_4}$) as a function of the calculated concentration of monoterpene oxidation products during the growth time. The ambient temperature during the growth time is indicated with the color.

correlation between sulfuric acid and oxidized organic concentrations ($r = -0.57$, $p << 0.001$) due to their different annual cycles. The former of these correlations is a consequence of the calculated $GR_{H_2SO_4}$ depending linearly on the sulfuric acid concentration and the variation in the ratio $GR_{H_2SO_4}/GR_{1.5-3}$, thus, being strongly controlled by the sulfuric acid concentration.

The difference between the observed growth rate ($GR_{1.5-3}$) and growth rate calculated from the sulfuric acid condensation ($GR_{H_2SO_4}$) did not tend to increase with an increasing calculated concentration of the oxidized organic compounds (Fig. 4). However, this does not mean that organic compounds could not explain the remaining growth. In previous studies, indications of oxidized organics playing a major role in the growth of particles larger than 3 nm in Hyytiälä has been found. Dal Maso *et al*. (2005) reported a seasonal variation of growth rates with a maximum in summer, indicating an important role of organics in the growth. Yli-Juuti *et al*. (2011) suggested that the concentrations of the volatile organic precursor gases may be limiting the particle growth. Peräkylä *et al*. (2014) suggested that the growth rate was linked to the monoterpene oxidation by ozone during the preceding night. There are several possible reasons why the connection between the growth rate and organic compounds remains hidden in this analysis of the smallest particles. Numerous organic compounds with different properties, e.g. saturation vapor pressures, could be condensing with varying contributions distorting the linear correlation between gas phase concentration and growth rate. The very small size of the particles emphasizes the effect of saturation vapor pressures. The various compounds could also interact in the particle phase which could affect the growth (Riipinen *et al*. 2012). Furthermore, the parameterization of the oxidized organic concentrations used in this study is a simplification and may not capture the concentrations exactly. However, such simplified approach was necessary to have a large enough data set for the analysis. The parametrization for the oxidized organic compounds was based on the first-generation oxidation products of monoterpenes. This may cause an overestimation of the oxidized organic concentration, since not all of the oxidation products are low enough in volatility to condense onto nanoparticles or go through fast subsequent oxidation reactions which would lower their volatility. The factor by which the condensable organic concentration is overestimated may also vary with ambient conditions. Finally, it is worth noting that experimentally-determined growth rates of ambient particles are subject to method-related uncertainties. The uncertainty in GR values is the greatest for the smallest particle sizes for the method used in this study, and this uncertainty might reflect also to the analysis presented here and hide some of the connections between the studied parameters.

The average ambient conditions during the 1.5–3 nm growth time (time from which growth rate was determined ± one hour) for the cases when pure sulfuric acid condensation could explain small (less than 10%) or large (more than 20%) fraction of the observed growth were compared (Table 1). Such a division showed the same behavior as above: The cases when sulfuric acid could theoretically explain a large fraction of the growth occurred at higher sulfuric acid concentrations and relative humidities, and at lower temperatures, UVB radiation intensities and concentrations of monoterpenes and oxidized organic compounds compared with the cases when sulfuric acid condensation could explain only a small fraction of the growth. This is related to the seasonal variation of these ambient variables.

Conclusions

Here, we presented growth rates of atmospheric

Table 1. Mean ambient condition during the sub-3 nm particle growth time for days when pure sulfuric acid condensation could explain less than 10% or more than 20% of the observed growth rate of sub-3 nm particles ($GR_{1.5–3}$). Also observed growth rates of 3–7 nm ($GR_{3–7}$) and 7–20 nm ($GR_{7–20}$) particles are given. Medians are given in parenthesis.

	$GR_{H_2SO_4}/GR_{1.5–3} < 0.10$	$GR_{H_2SO_4}/GR_{1.5–3} > 0.20$
$[H_2SO_4]$, calculated (cm^{-3})	1.5×10^6 (1.3×10^6)	10.1×10^6 (8.4×10^6)
Relative humidity (%)	49.5 (49.4)	57.1 (53.5)
T (°C)	7.8 (8.9)	-1.8 (-1.3)
UVB (W m^{-2})	1.1 (1.1)	0.8 (0.7)
[OxMT], calculated (cm^{-3})	1.7×10^8 (1.5×10^8)	0.8×10^8 (0.5×10^8)
[MT], calculated (cm^{-3})	3.4×10^9 ($3.2 \cdot 10^9$)	1.8×10^9 (1.5×10^9)
$GR_{1.5–3}$ (nm h^{-1})	2.6 (2.1)	1.5 (1.5)
$GR_{3–7}$ (nm h^{-1})	4.1 (3.7)	3.5 (3.1)
$GR_{7–20}$ (nm h^{-1})	5.4 (4.0)	3.7 (3.2)
Number of days	168	42

sub-3 nm particles at Hyytiälä for years 2003–2013 and compared them with the theoretically-predicted growth rates from condensation of sulfuric acid along with other ambient parameters. The analysis of ambient sub-3 nm growth rates are crucial to understanding the gas-to-particle conversion in the atmosphere (e.g. Kulmala *et al*. 2014).

On average, sulfuric acid condensation could theoretically explain 7.4% (median) of the observed particle growth. Therefore, it seems unlikely that the main process causing the growth was condensation of sulfuric acid monomers. Furthermore, the measured growth rate did not correlate strongly with the sulfuric acid concentration, even though a weak increase in the values of $GR_{1.5–3}$ was seen with an increasing sulfuric acid concentration. This result is different as compared with that of the laboratory study by Lehtipalo *et al*. (2016), where a strong correlation between the growth rate and sulfuric acid concentration was seen although the gas phase sulfuric acid concentration was too low to explain the observed growth rate. Lehtipalo *et al*. (2016) performed the chamber experiments at atmospherically relevant sulfuric acid concentrations without oxidized organic vapors and concluded that their laboratory observation was explained by the coagulation of sulfuric acid-containing clusters with the growing particles. The reason for this difference between ambient and laboratory observations can be speculated to be that sulfuric acid clusters do not provide a considerable pool of hidden sulfuric acid for the growth in the studied ambient conditions, or that at least this effect is shadowed by other compounds or processes. This seems possible because gas phase amine concentrations may be pretty small (< 1 pptV) in a boreal forest (Sipilä *et al*. 2015).

Neither particle growth rate nor the fraction of growth explained by sulfuric acid showed a clear connection with organic concentration. On the other hand, enough low-volatile (or even extremely low-volatile) organic compounds have been detected in the ambient boreal forest air to explain the growth at least on some days (Kulmala *et al*. 2013, Ehn *et al*. 2014). Since sulfuric acid could not explain the observed growth alone, the results may suggest that both sulfuric acid and organics play an important role in the growth. However, both sulfuric acid and oxidized organics concentrations were based on estimates instead of direct measurements, and probably these estimates — particularly for organics — are not accurate enough to see the growth dynamics. Therefore, existing connections between organic compounds' gas phase concentrations and growth rates were shadowed in the current study due to the uncertainties related to the estimation of sulfuric acid and particularly organic acid concentrations. Such estimation methods and improvement of them are currently needed, when analysis of long atmospheric data time series are desired. It is clear, however, that the growth of sub-3 nm particles and organic compounds condensing on them remain an important research question.

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